Synthesis of Novel Forward Osmosis membrane with Nanoparticle blended support layer

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Synthesis of Novel Forward Osmosis membrane with Nanoparticle blended support layer

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LIST OF ABBREVIATION

PVDF	Polyvinylidene fluoride
PSf	Polysulfone
TMC	Trimesoyl chloride
MPD	m-Phenylenediamine
NaCl	Sodium chloride
GO	Graphene oxide
MOS_2	Molybdenum disulfide
FO	Forward osmosis
RO	Reverse osmosis
PRO	Pressure-retarded osmosis
UF	Ultrafiltration
NMP	N-Methyl-2-pyrrolidone
DMF	Dimethylformamide
TFC	Thin film composite
ECP	External concentration polarization
ICP	Internal concentration polarization
S	Structure parameter
LMH	Liter per square meter per hour
GMH	Gram per square meter per hour

SUMMARY

Compared to conventional pressure-driven membrane separation processes like ultrafiltration and reverse osmosis, forward osmosis technology inherently has many unique advantages, such as low pressure or even no pressure operation. Wastewater were almost wholly intercepted, resulting in low membrane fouling characteristics and good separation effect.

My thesis focused on the improvement of the material in forward osmosis membrane. By blending GO and MOS_2 which are high tortuosity nanoparticles with polymer materials such as PVDF and PSf, we enhanced the structural coefficient and hydrophilicity of the membrane. The blending further increased the flux while maintaining high retention and reduced internal concentration polarization and pollution. The changings of the percentages of GO and MOS_2 cause the difference of performance. The higher loading of GO is favorable to membrane performance, but the loading of MOS_2 is not. The performance is good only at 0.05%wt and 1%wt, higher or

lower loading would bad for performance. This work demonstrated that the FO membrane has a good potential application in seawater desalination, drinking water and wastewater treatment.

Chapter 1

Introduction

Osmosis is a physical phenomenon that has been exploited for many years by human-being such as the observation of pickled products which could make the foods have a longer shelf life. In the water treatment area, osmosis is the transport of water across a selectively permeable membrane from a region of higher water chemical potential to a region of lower water chemical potential. It is driven by a difference in solute concentrations across the membrane that allows the passage of water and rejects most solute molecules or ions [1]. Usually, we define the higher water chemical potential side as draw solution, the lower water chemical potential side as feed solution.

The osmotic pressure (π) is the minimum pressure which needs to be applied to a solution to prevent the inward flow of its pure solvent across a semipermeable membrane[2]. Also, we defined the applied pressure as P, the difference osmotic pressure between the membrane as $\Delta\pi$, the difference applied pressure between the membrane as ΔP According to the comparison between $\Delta\pi$ and ΔP, we could divide the

osmosis process as Forward Osmosis which means $\Delta\pi$ is larger than ΔP and Reverse Osmosis which means $\Delta\pi$ is smaller than ΔP. Reverse osmosis is currently the dominant water treatment such as water desalination technology. Reverse osmosis is hard to see its future potential because RO needs a very high hydraulic pressure which is provided by consuming a vast amount of energy and money to run the whole process. Comparing to reverse osmosis; FO offers recognized advantages including high rejections to contaminants, low operating pressure and temperature, potentially low fouling and less energy consumption. Therefore, FO membranes have great potential to replace the ultrafiltration (UF) membrane currently used in the membrane bioreactor (MBR) for water reuse[3]. Because of these advantages, the FO is more environmentally friendly.

Between the FO and RO, there is an intermediate osmosis process called Pressure retarded osmosis (PRO). In PRO process, the hydraulic pressured is applied at the draw solution side which is same as RO, but this pressure is less than the osmotic pressure. However, I prefer to classify it as FO because the water flux direction is the same as FO. There is a general equation to describe three

osmosis process:

$$J = A\ (\Delta\pi - \Delta P)$$

Where J is the pure water flux, A is the water permeability coefficient of the membrane, $\Delta\pi$ is the osmotic pressure difference across the membrane, ΔP is the hydraulic pressure difference across the membrane.

To give a straightforward view, Figure 1 was given.

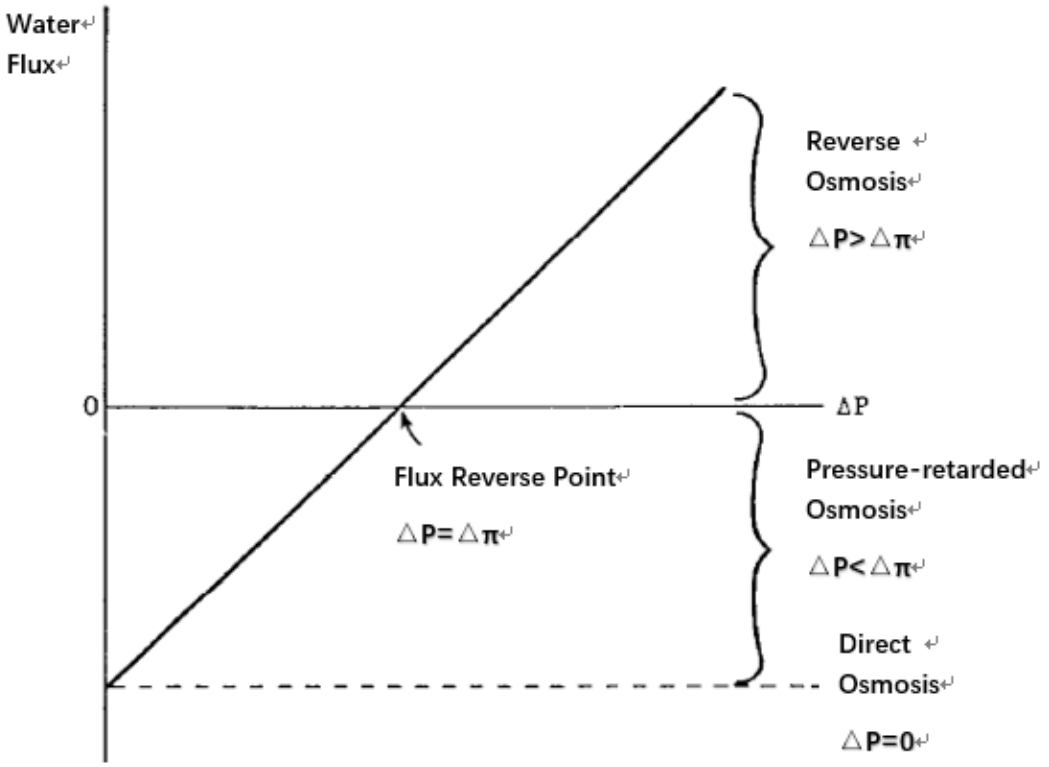


Figure. 1. The relationship between FO (Shown as DO), RO and PRO for an ideal semipermeable membrane [4].

Separation membranes are made up of two layers: Support layer and active layer. The support layer is a thick and porous layer which can provide substantial support and affect the mechanical performance of the membrane. On the contrast, the active layer is a thin and dense layer which can provide the selectivity and affect the separation performance of the membrane. Figure 2 shows a typical structure of the membrane.

Figure 2: Common structure of separation membrane

Usually, we first fabricated the support layer and then add the active layer. To fabricate the support layer, there are two widely-used methods: phase inversion and electrospinning. Phase inversion is a process of controlled polymer transformation from a liquid phase to solid phase. To fabricate the active layer, we usually

use interfacial polymerization.

Membrane performance is usually evaluated by two factors: selectivity and permeability. There is always a trade-off effect between them. It is hard to achieve both high selectivity and permeability at the same time. What we want to focus is to synthesize novel FO membrane to enhance both high selectivity and permeability membrane.

Chapter 2

Literature Review

To start my research, I did an extensive literature review. The first part is to select the membrane materials. The directions for development of new membrane materials are very promising in the future, primarily because the enormous chemical flexibility and permeability of the membrane base structures can be improved.

The separation properties of the membrane can be tuned, as can operational parameters such as stability and longevity. Besides, functional additives such as involved selective agents can be incorporated into these new classes of membrane materials, providing exciting new opportunities for enhancing separation performance [5].

Polyvinylidene fluoride (PVDF) is a desirable membrane material due to its chemically inert property, along with excellent physical and thermal stability. It is widely used in the filtration process [6] [7]. To date, most of the commercial PVDF separating membranes including the FO membrane are produced via the phase inversion method due

to the simplicity and flexible production scales of its process [8][9].

What is more, Polysulfone (PSf) membranes have become particularly frequent in the past years. PSf films have the inherent advantage that they apply to a wide range of pH and temperature (up to 105℃). They are also resistant to chlorine oxidation [10] [11].

Some other material such as polyvinyl chloride may also be a suitable substrate material for FO membrane [12].

To prepare a FO membrane with high performance, it is convenient and efficient to introduce some more suitable additives as pore former into the casting solution to control membrane structure and morphology [13]. It is noted that almost the major existing applications of nanocomposites are in the active layer or act like the whole support layer, and their effects have been reported in the previous publication [14] [15] [16].

In our group, we have done such these addition of nanoparticles like methacrylate (PEGMA) in ultrafiltration membrane to get high performance exceptionally high water flux [17] [18].

For the membrane process, the primary challenge is the fouling. Fouling comes from two major problems: External concentration polarization (ECP) which is easy to be solved and Internal concentration polarization (ICP) which is the severe problem occurs inside the porous support layer. The ICP leads to a sharp reduction of water flux and it could be influenced by the porosity, tortuosity and the thickness [19] [20]. Also, the hydrophilic membrane like sulphonated poly (ether ketone) (SPEK), sulfonated poly (ether ether ketone) (SPEEK), polydopamine (PDA) or hydrophobic membrane like PVDF, polyacrylonitrile (PAN) could also affect the fouling degree [21] [22] [23]. We could use structure parameter S to measure the ICP degree.

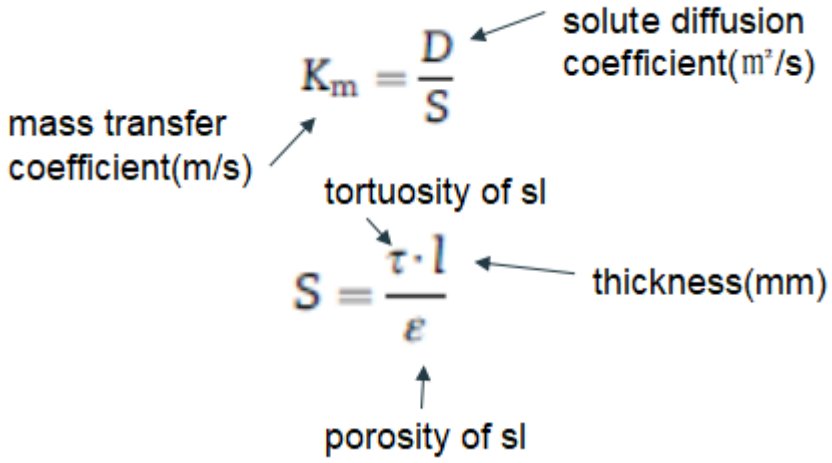


Figure. 3 Calculation of membrane structure parameter(S)

For S, the lower, the better. An ideal support layer for the FO membrane should be low tortuosity, high porous and a comparable thin structure. To reduce to S value is the significant task in membrane research not only in FO but also in other water filtration process [24].

To reduce the S, some work has been done by other researchers. There is significant research that gives the propose of thin film composite (TFC) theory. The top active layer formed by interfacial polymerization and the support layer fabricated via phase inversion. Under the process of casting support layer, some key factors were focused such as solvent quality, dope polymer concentration, fabric layer wetting and even the casting blade gate height [25]. Also, there are some works focus on the structure change. Three-tier thin film composite was applied to FO membrane. The membrane has three layers: two active layers at the top and the bottom, on the support layer on the middle. Two active layers were formed by interfacial polymerization and network composite nanofibers which could be made hydrophobic or hydrophilic [26] [27]. This method could also be used in

emulsified oil-water separation process and heavy metal ions water treatment. The polyamide layer face to the draw solution that composed by NaCl Solution, and the thin copolymer layer face to the feed solution that comprised of the oil-water solution. The application of this kind of double-skinned membrane could both gives a very dense skin for salt rejection and a loose dense skin for emulsified oil particle rejection [28] [29] [30] [31].

On a small scale, the pore is the membrane's core. How to build membrane nanopores is crucial important [32]. To get an ideal pore size and pore structure is a challenge. There are two kinds of pore structure: finger-like pore structure and spongy-like pore structure. The first one has low tortuosity and high porosity that make it has a low structure parameter [33]. This is the ideal pore structure we want. Also, the impact of nanoparticles surface characteristics on pore structure could not be overlooked [34].

More details on condition control under lab scale need us to pay attention to. First one the effects of feed and draw solution temperature and transmembrane temperature

difference. Also, the monomer concentration has an impact on membrane performance. What's more, the direction between the membrane and water solution could be considered. AL-FS means the active layer face to feed solution, is commonly accepted in FO due to low fouling behavior. Also, the direction of feed solution and draw solution. Co-current and counter-current flow configuration give the different results. The last is the water recovery. Water scarcity always affects people throughout the world. If we could let the fouling fully reversible, with almost 99% recovery of permeate water flux possible only after pure water rinses rather than adding chemical reagents, it would change the world [35] [36] [37] [38] [39].

CHAPTER 3

METHODOLOGY

3.1 Experimental Design

Based on my comprehensive literature survey and my previous experience on PVDF ultrafiltration membrane in the lab [40], I designed my master thesis topic and experiments with the help from Ms. Su.

Our group and my previous research indicated PVDF is good material in the ultrafiltration membrane. Base on its property, I selected it to use as an optional support layer material. Conventional support layer polymer material PSf is also be used as a comparison. Phase inversion was applied as the fabrication method of the support layer. Also, I tried the electrospinning method but decide to not use it due to low efficiency and stability. The solution I used is N-Methyl-2-pyrrolidone (NMP). The other solution Dimethylformamide (DMF) was applied in ultrafiltration membrane as PVDF solution. Base on the literature review, NMP is the better solution for NMP and nanoparticles. To control the variable, I selected NMP as the solution. Last, as I mentioned

before, the concentration of the casting solution is critical. Base on the literature review, I opted to the proper range of polymer content.

The second step was to blend nanoparticles in the casting solution. For the selection of nanoparticles, by the inspiration of current hot works, I selected the Graphene oxide (GO) and Molybdenum disulfide (MoS_2). Their 2D structure properties like sizeable specific surface area, high electrical and thermal conductivity, optical transparency, and substantial mechanical strength combined with inherent flexibility were potentially useful in FO membrane [41]. To fabricate the active layer, I used the common method interfacial polymerization to form polyamide on the top of the support layer.

3.2 Materials and method

3.2.1 Materials:

PVDF powder (average Mw-534,000 by GPC) and PSf particles (average Mw ~35,000 by LS) were purchased from ALDRICH Chemistry.

GO particles was cut from GO nanosheets which made by

ourselves by a chemical exfoliation technique. MoS_2 powder (<2μm, 99%), TMC powder (98%) and MPD powder (flakes, 99%) were purchased from ALDRICH Chemistry

Hexane (anhydrous, 95%), NMP (anhydrous, 99.5%) and NaCl (BioXtra, >99.5%) were purchased from SIGMA-ALDRICH.

3.2.2 Method

3.2.2.1 Support layer fabrication

The fabrication process of the PVDF support layer:

First, PVDF or PSf (9%wt, 12%wt, 15%wt and 20%wt) were added to the NMP. After the powder was completely dissolved in the NMP, slowly added GO(0-1.5%wt) or MoS_2(0-2%wt) to the mixture with high-speed stirring. The order of addition could not be changed. According to the experiments, if I first added the nanoparticles then added the polymer, it was not going to completely dissolve in NMP which means the casting solution could not be formed. After all nanoparticles were added, continue stirred for 12-24h until a homogeneous solution was developed. Then, the polymer suspension was held static for at least six hours to get rid of the air bubbles before use. Prepared the water bath with DI water

before casting membranes to control the temperature. If the temperature was different, the morphology was going to change. Usually, the temperature was set as room temperature 25℃. Then adjusted the thickness of the casting blade. The membranes were cast on a glass plate with the thickness of 150 μm, 175 μm and 200 μm. The glass quickly be immersed in a deionized water coagulation bed smoothly to conduct the phase inversion step. All the membranes were kept in an aqueous bath for at least six hours to remove residual reagents before the next modification.

For PSf(9%wt) the support layer, there was a little difference. First, PSf was much easier to dissolve in NMP, so the stirring time could be decreased. Second, PSf solution was easy to precipitation and had less risky to get the bubble. I had to stir it for a short time to make the solution homogeneous.

3.2.2.2 PA active layer preparation

To fabricate the active layer of the FO membrane, almost every previous researcher was using the interfacial polymerization. 1.5%wt m-Phenylenediamine (MPD) solution

was prepared with DI water solution and 0.15%wt trimesoyl chloride (TMC) was prepared with hexane solution. To promote TMC dissolution process, we must put the TMC solution in the ultrasonic generator for about 1 hours and then shook it to get the 0.15%wt TMC solution. The amounts of MPD and TMC could be changed based on the thickness of the active layer. Next step was to pour MPD solution into a membrane holder and the membrane was rinsed for at least 3 min. The membrane surface should be dried until no water left, and then poured TMC on the surface to finish the interfacial polymerization process. At last, the membrane was placed into a 60 ℃ oven for 1 min, and then stored in DI water at least 12 hours for testing.

3.2.2.3 Membrane characterizations

Porosity: The membrane porosity **ε**(%) is defined as the ratio of the volume of pores to the total volume of the membrane, and in this study, it was determined by the wet-dry weighting method. The wet membranes to be tested were cut into small pieces and weighted after mopping shallow water. Then these samples were put into a vacuum oven at 60 ℃ until there was no change in weight. Therefore, **ε** was

determined by the following equation:

$$\varepsilon = \frac{(w_W - w_D)/\rho_W}{(w_W - w_D)/\rho_W + w_D/\rho_M} \times 100\%$$

The equation of calculation of membrane porosity

Where W_W is the weight of wet membrane (g), W_D is the weight of dry membrane (g), ρ_W is the pure water density, and ρ_M is the density of composite membrane. For each membrane, three samples were tested at least three times and getting an average value.

Fourier transform infrared spectroscopy (FTIR) spectra was the range from 500 to 4000 cm^{-1}. Membrane samples were also dried at the same conditions as above (at 60℃ in a vacuum oven) before the FTIR analyses. The surface morphology of membrane was viewed scanning electron microscope (SEM) under magnifications ranging from 5,000 to 20,000, and the samples were successively sputter coated with a thin gold film before SEM observation. I did several times SEM in the experiment, some were sputter coated with a thin gold film, but most were not because the image can let me figure out the structure of membrane I want. Of

course, covered with a thin gold film was a better and general method. Also, the next to be tested later was the tensile strengths of the membranes which could be measured by an electromechanical universal testing machine. Wet membranes were cut into the standard shape for tensile strength measurements. The strength at break and elongation was measured in ambient condition for at least three samples, and the average value was reported.

The membrane separation properties were measured by a home-made forward osmosis cell (effective area 10 cm^2, cross flow). I put the membrane in the cell with AL-FS direction. The pure water flux of membrane was determined at different transmembrane pressures which were provided by the concentration difference between the draw solution and feed solution. For each concentration, the membrane was first rinsed in pure water for 1 hour and then compacted for 10 minutes to minimize compaction effects. After the flux reached a steady state, the flux was calculated:

$$\mathbf{F= V/(A*t)}$$

Pure Water Flux calculation

$$\mathbf{F_s=M/(A*t)}$$

Reverse Salt Flux calculation

Where F is the pure water flux (L/m^2 h), V is the permeate volume (L), A is the membrane area (m^2), and t is the time (h). F_s is the reverse salt flux (G/m^2 h), M is the reverse salt weight (G), A is the membrane area (m^2), and t is the time (h).

The draw solution was set as the fixed concentration of 0.5M, 1M, 1.5M, and 2M. To monitor the reverse salt flux, the conductivity meter was used to measure the conductivity in the feed solution. Base on the conductivity-concentration curve, I could find the concentration in the feed solution.

CHAPTER 4

RESULTS

4.1 Experimental Evaluations

4.1.1 GO flake characterization

To get the SEM pictures, modified GO membranes were diluted with DI water and cut into small strips to test their structures.

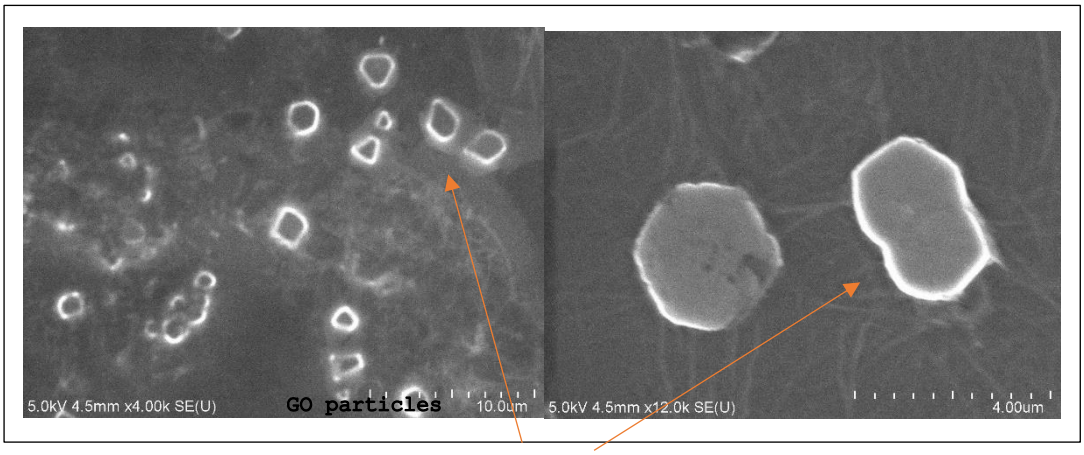


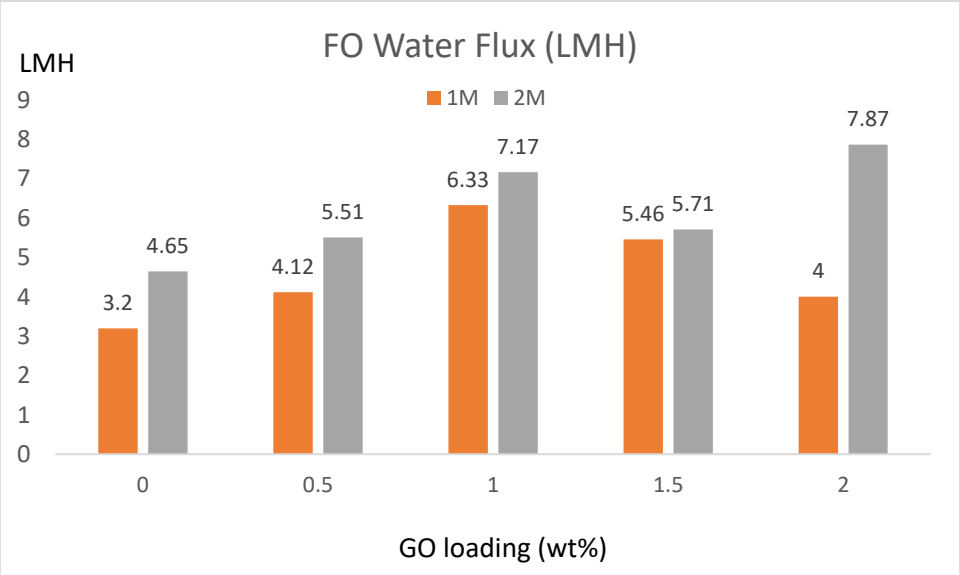
Figure 4 GO flake cross section under SEM in different solution

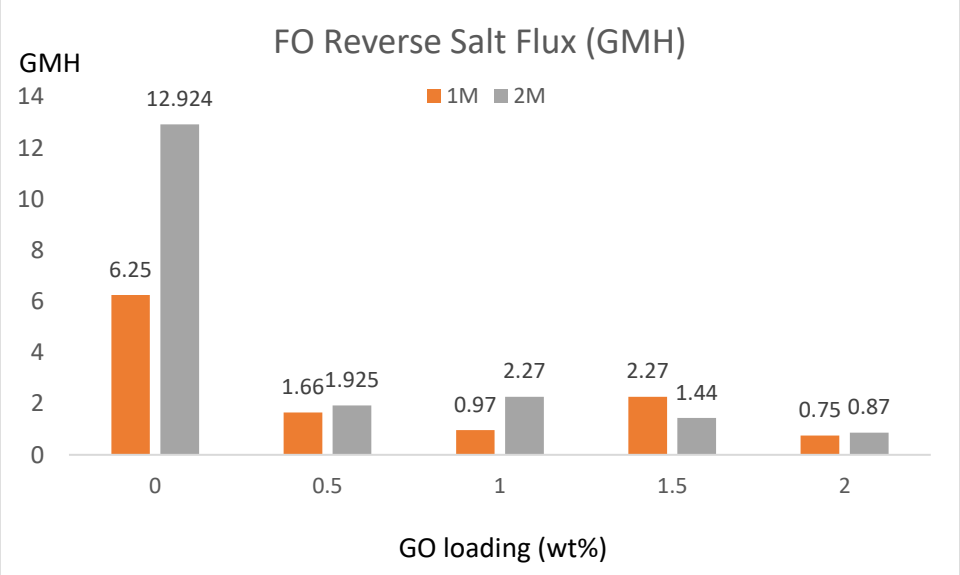
The picture showed that the GO particles were well-dispersed in the membrane without visible aggregation.

MoS_2 was much easier to be dissolved in solution, so I did not get the SEM image.

4.1.2 PVDF-GO membrane performance

4.1.2.1 Water flux and reverse salt flux





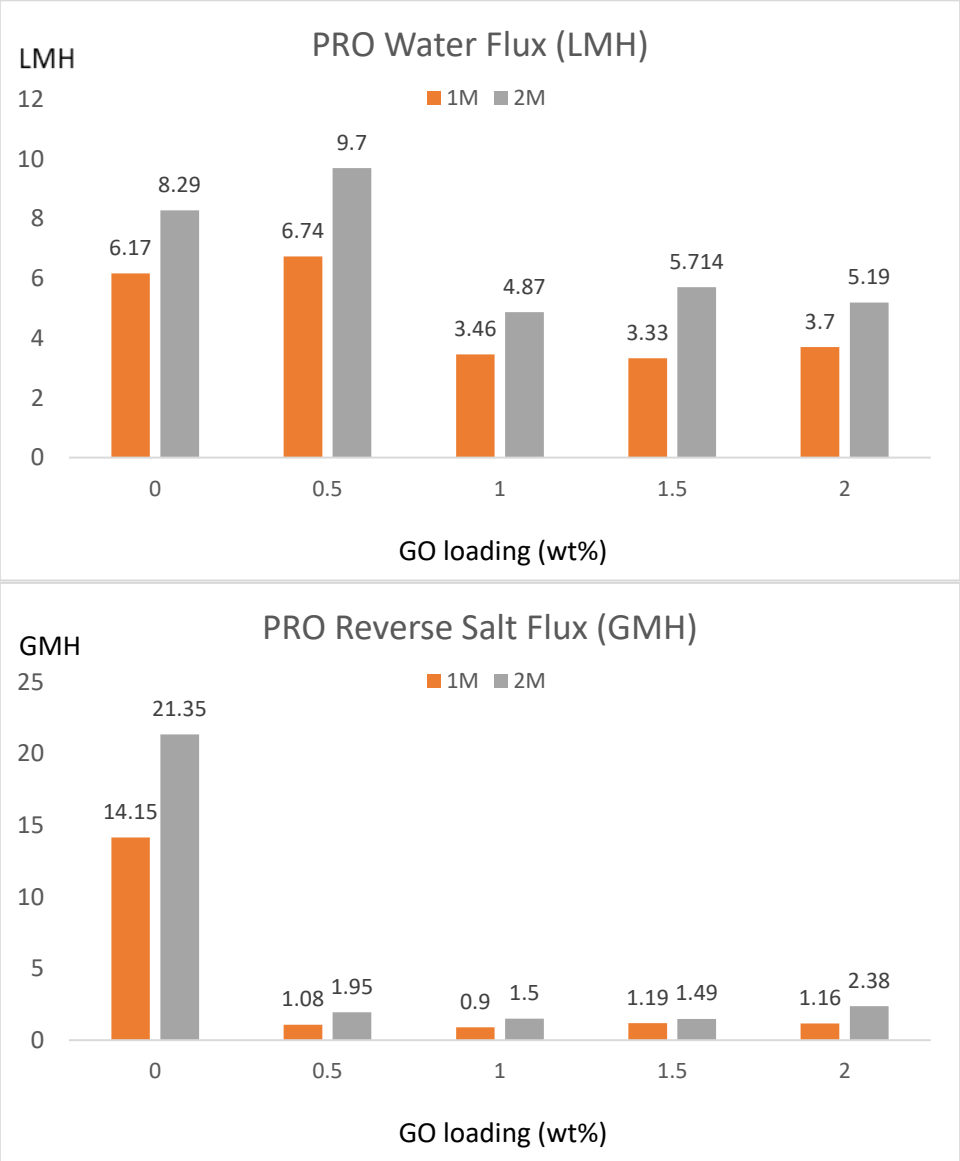


Figure 5 Membrane pure water flux and reverse salt flux results under 1M and 2M draw solution in FO and PRO systems.

After adding GO particles, pure water flux increased when loading dosages at 1%wt and 2%wt were added into nanocomposite support layer of the FO membranes. At1%wt GO dosage, GO-PVDF-PA exhibited the best performance in FO

mode with a pure water flux of 6.33 LMH, under the condition of 1M NaCl draw solution with the reverse salt flux of 0.97 GMH. At 2%wt dosage, GO-PVDF-PA exhibited the best performance in FO mode with a pure water flux of 7.9 LMH, under the conditions of 2M NaCl draw solution with the reverse salt flux of 0.87 GMH. Overall, in both FO and PRO mode, pure water flux did not change significantly after adding GO, but still larger than transparent PVDF membrane. However, to date, the result suggested a key finding that the reverse salt flux remarkably decreased after GO addition. Almost all the membranes with GO exhibited very low reverse salt flux under 2 GMH. When GO loading was higher, the reverse salt flux became lower. The lowest reverse salt flux was only 1/15 as compared with the transparent PVDF membrane. Under this condition, the FO membrane could have a longer lifetime with little fouling.

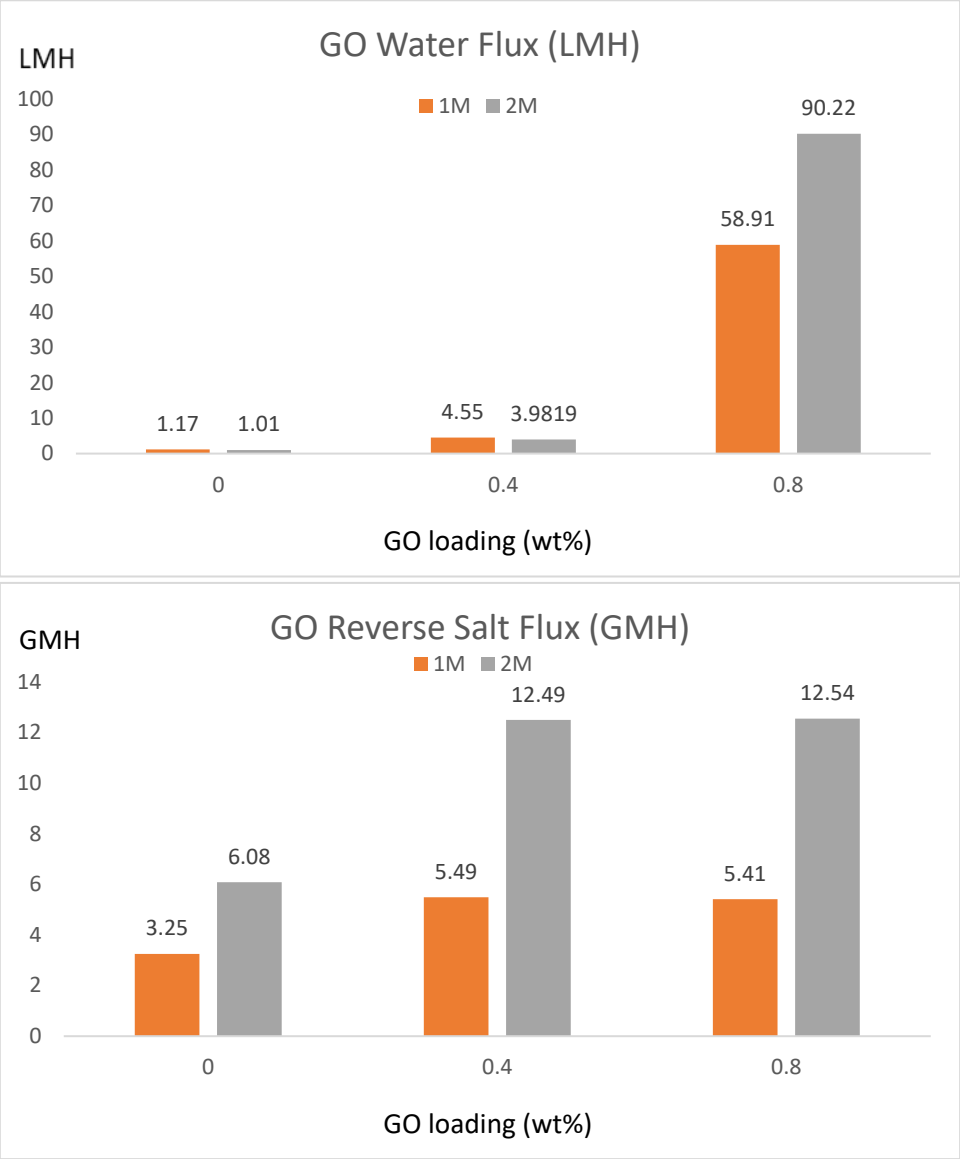
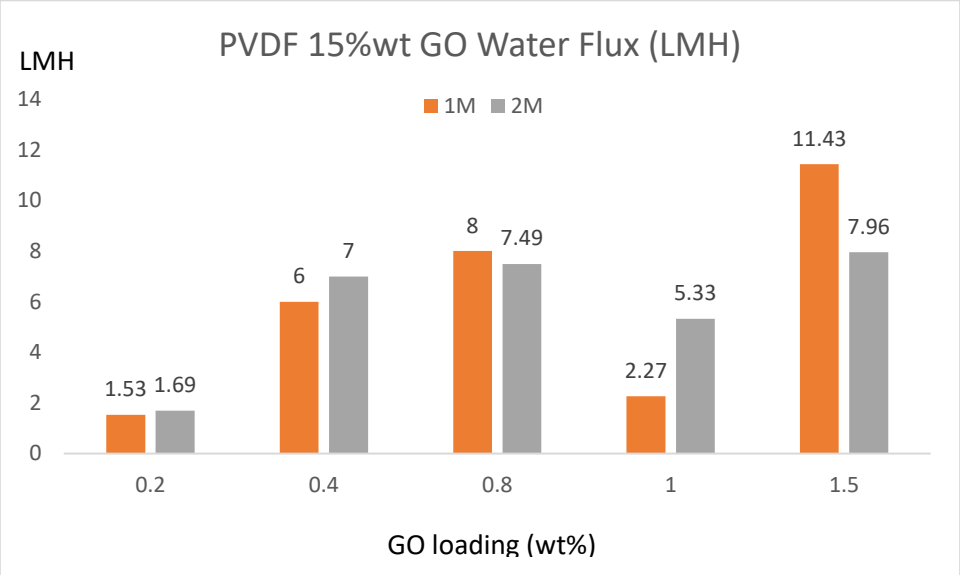


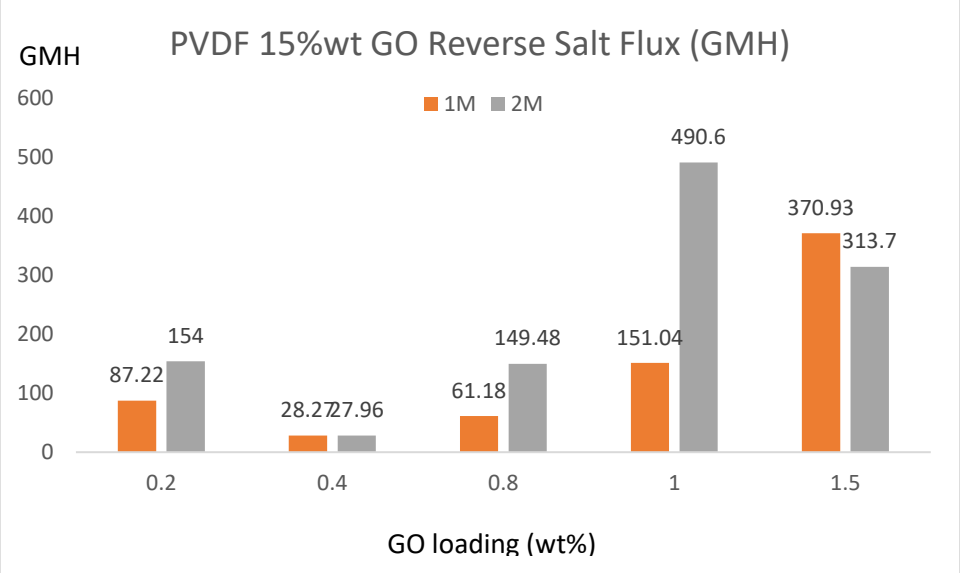
Figure 6 Membrane pure water flux and reverse salt flux results under 1M and 2M draw solution in FO system.

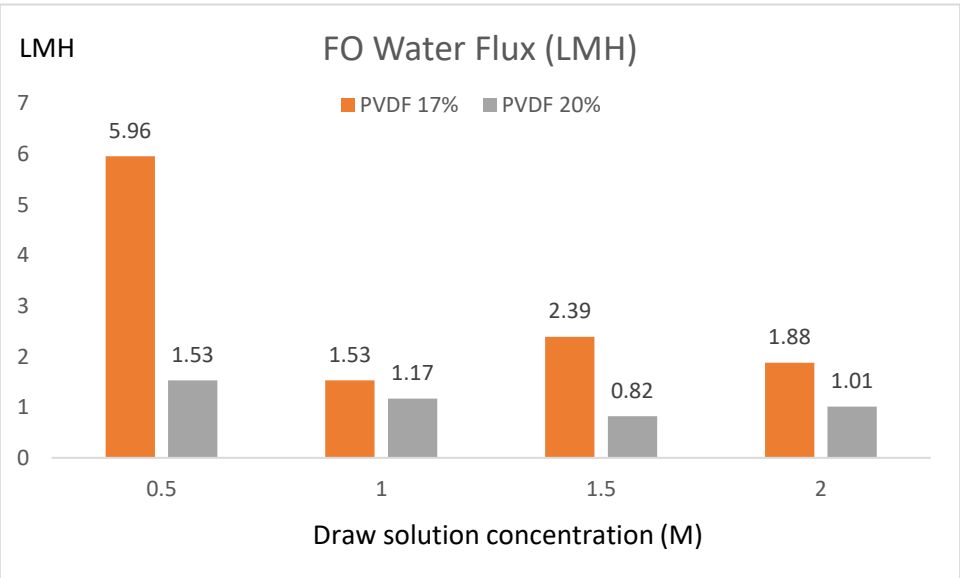
It could be seen in Figure 6 that the impacts of GO loadings at 0.4%wt and 0.8%wt were consistent with the previous conclusion that GO addition could result in a high water flux meanwhile a low reverse salt flux of the FO.

4.1.2.2 Different PVDF percentage performance

PVDF also exhibited an influence on the performance of the FO membrane. Figure 7 showed the results with different PVDF proportions, it was found that 20%wt was an ideal value for PVDF addition, which was accordance to the UF membrane as reported in previous works. The 15%wt PVDF showed the worst FO performance: a little increase of reverse salt flux, but very low water flux. From my point of view, it was because the concentration of PVDF was too low, so under the rush of salt water, the structure of membrane had been broken. The 17%wt PVDF membrane exhibited the sizeable reverse salt flux and general water flux. Although the 20%wt PVDF membrane alone had a low FO water flux, it performed a very low reverse salt flux. The blending of nanoparticles could significantly increase the water flux but make little contribution to reverse salt flux.


PVDF 15%wt GO Water Flux (LMH)
LMH
1M
2M
14
12
10
8
6
4
2
0
1.53
1.69
6
7
8
7.49
2.27
5.33
11.43
7.96
0.2
0.4
0.8
1
1.5
GO loading (wt%)


PVDF 15%wt GO Reverse Salt Flux (GMH)
GMH
1M
2M
600
500
400
300
200
100
0
87.22
154
28.27
27.96
61.18
149.48
151.04
490.6
370.93
313.7
0.2
0.4
0.8
1
1.5
GO loading (wt%)


FO Water Flux (LMH)
LMH
PVDF 17%
PVDF 20%
7
6
5
4
3
2
1
0
5.96
1.53
1.53
1.17
2.39
0.82
1.88
1.01
0.5
1
1.5
2
Draw solution concentration (M)

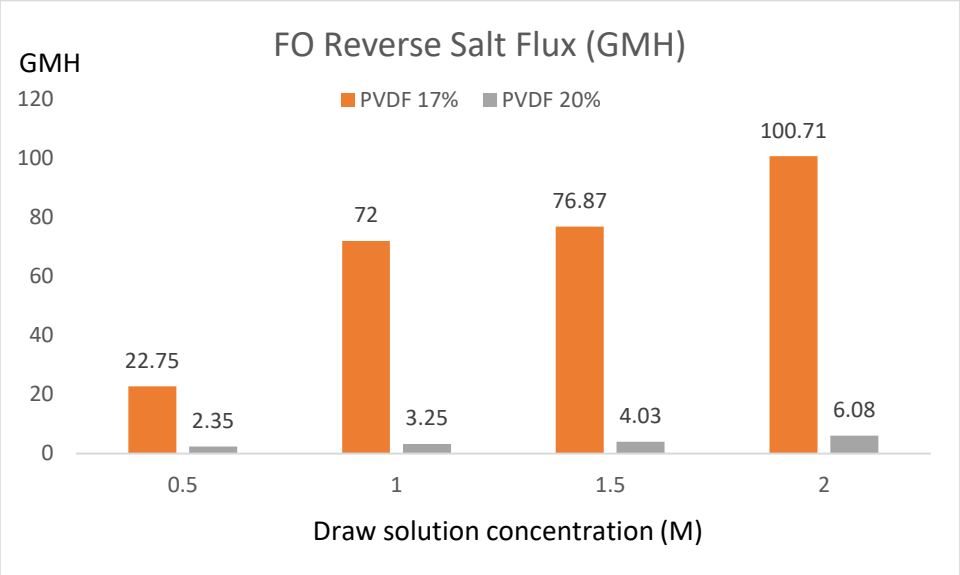
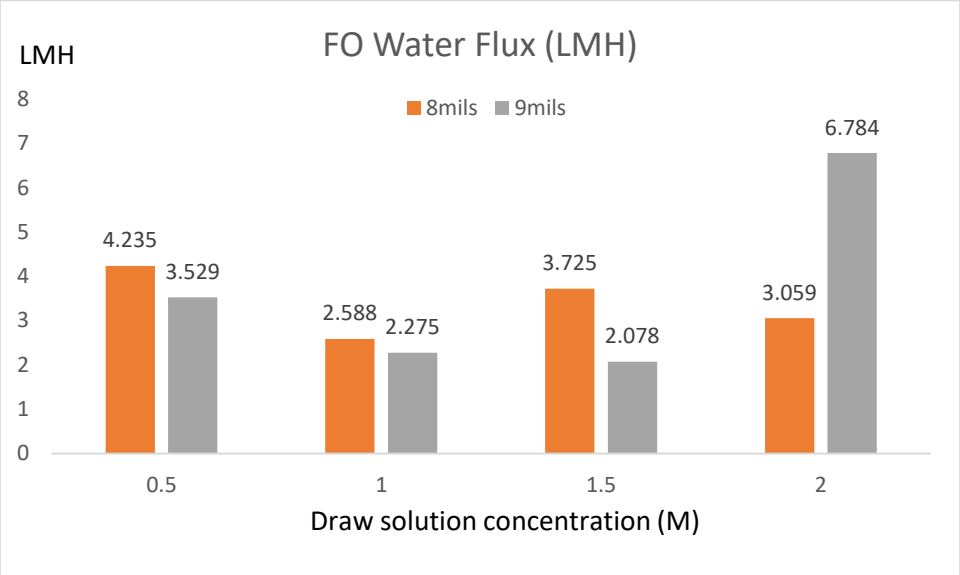
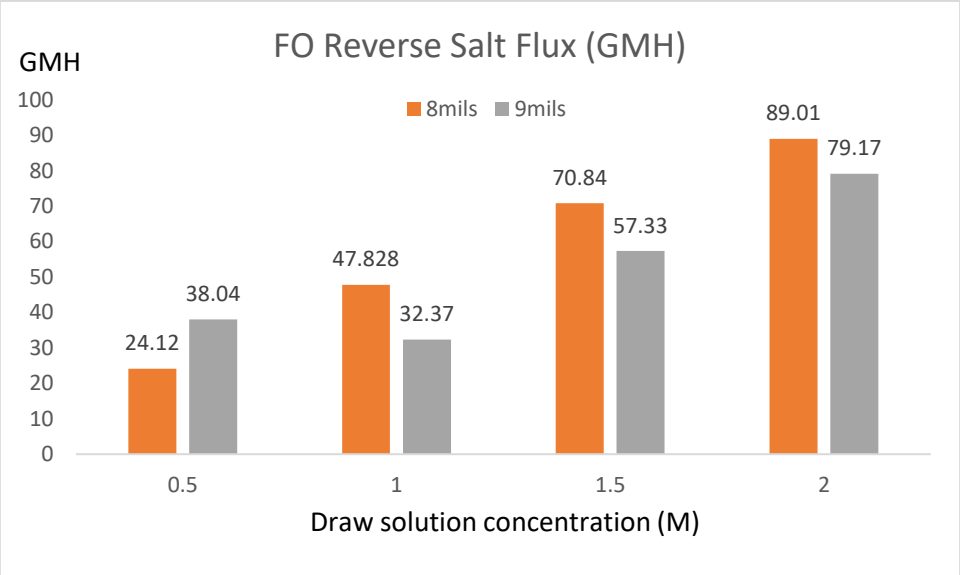


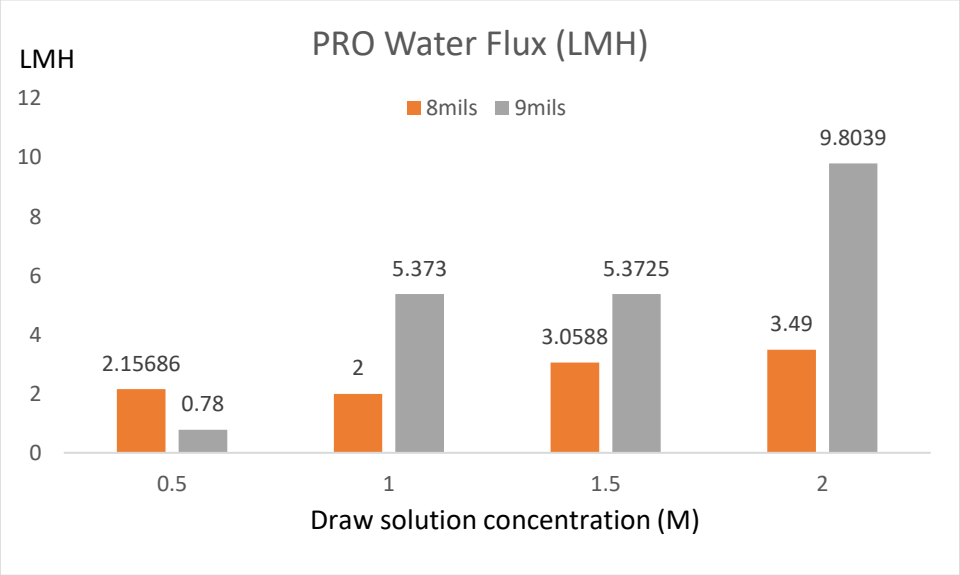
Figure 7 PVDF content impact on membrane performance

4.1.2.3 Different thickness membrane performance

What's more, after testing the membrane performance in different thickness, the thickness of 8 mils and 9 mils did not affect the FO performance, which was consistent with the results of literature reference. Accordingly, 8 mils was determined as the desirable thickness. The membrane thickness was fixed at 8 mils (203.2μm) in the following experiments.


FO Water Flux (LMH)
LMH
8mils
9mils
8
7
6
5
4
3
2
1
0
4.235
3.529
2.588
2.275
3.725
2.078
3.059
6.784
0.5
1
1.5
2
Draw solution concentration (M)


FO Reverse Salt Flux (GMH)
GMH
8mils
9mils
100
90
80
70
60
50
40
30
20
10
0
24.12
38.04
47.828
32.37
70.84
57.33
89.01
79.17
0.5
1
1.5
2
Draw solution concentration (M)


PRO Water Flux (LMH)
LMH
8mils
9mils
12
10
8
6
4
2
0
2.15686
0.78
2
5.373
3.0588
5.3725
3.49
9.8039
0.5
1
1.5
2
Draw solution concentration (M)

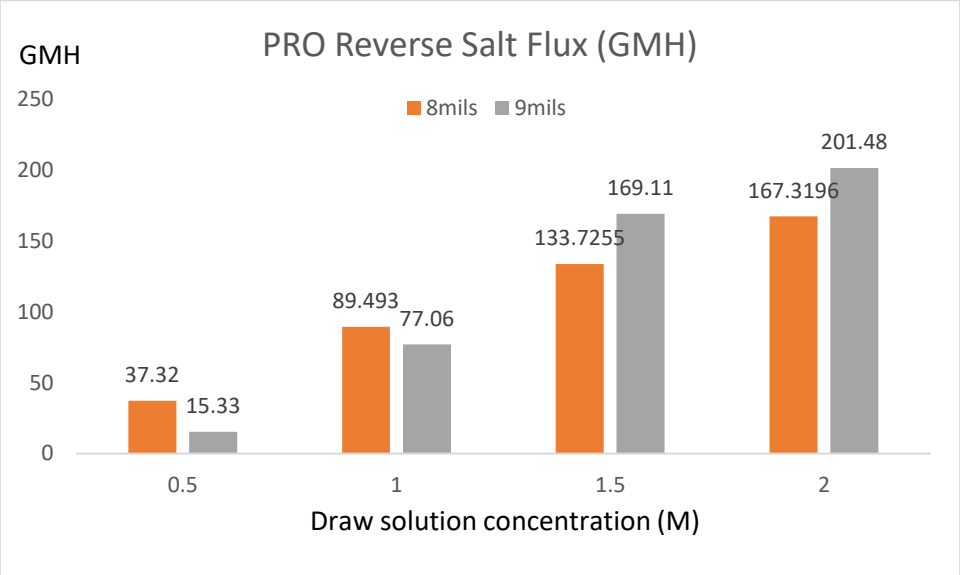


Figure 8 Thickness effects on membrane performance

4.1.2.4 Contact angle

The contact angle results are shown in Figure 9. After GO addition, the curves were decreased. It meant the hydrophilicity was enhanced. This was beneficial to inhibit the ICP in the FO membrane.

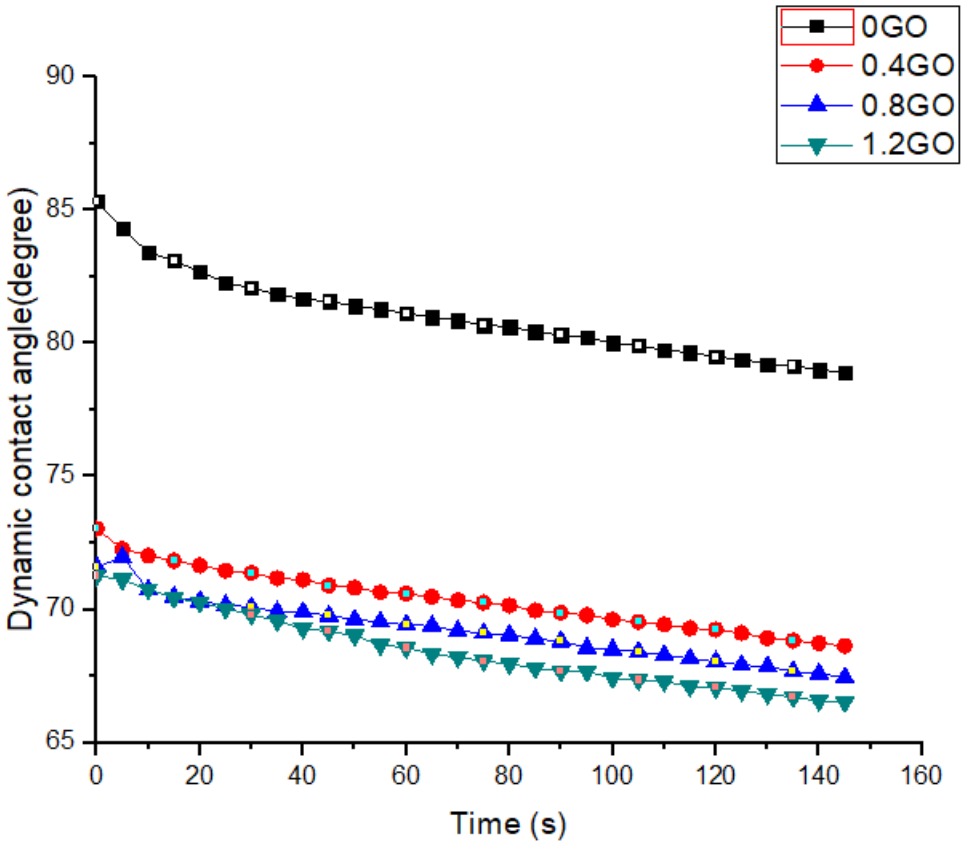
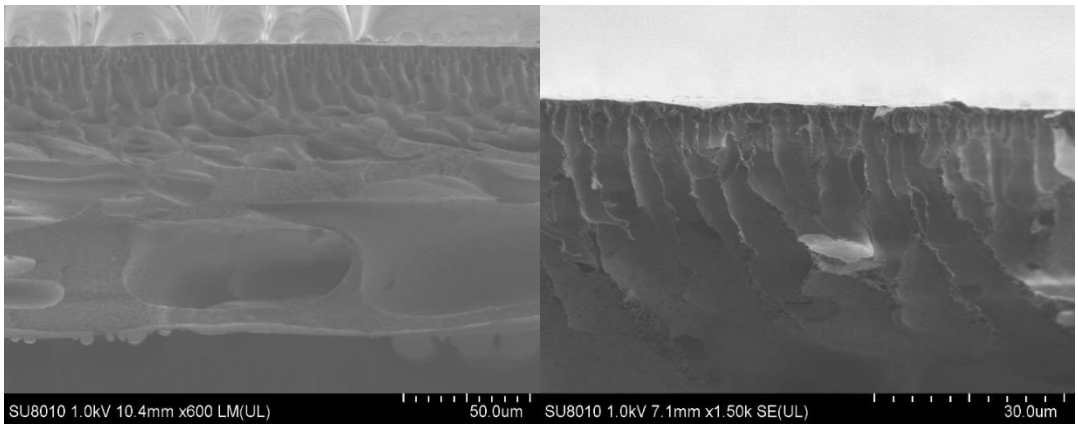


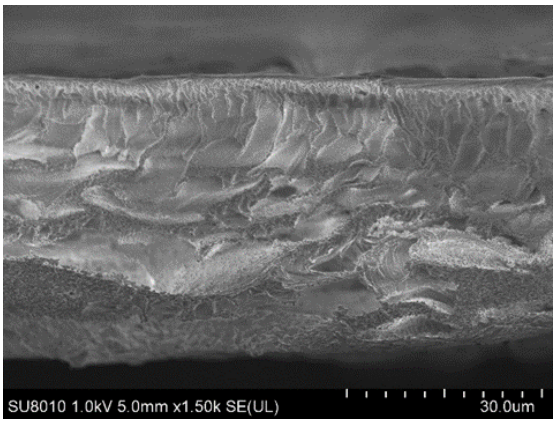
Figure 9 Contact angle data of PVDF-GO membrane

4.1.3 PSf-GO/MOS$_2$ membrane performance

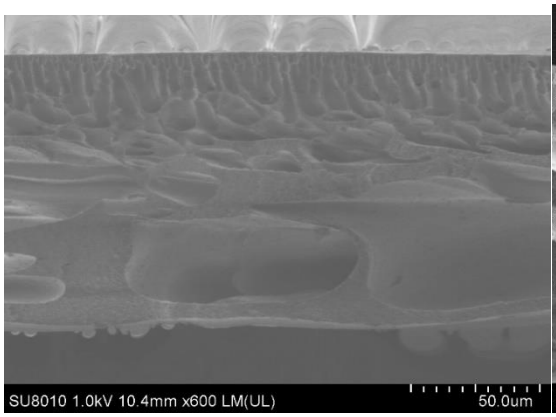
4.1.3.1 SEM images



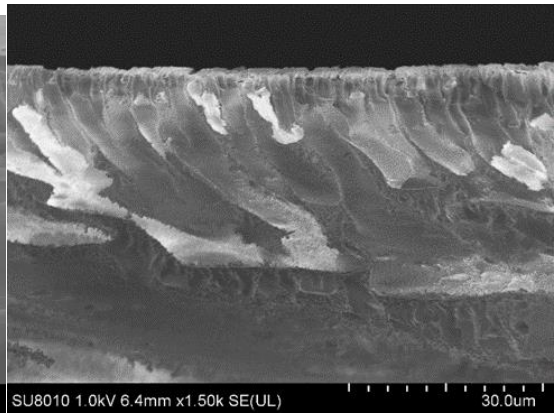
a 0%wt GO b 0%wt GO



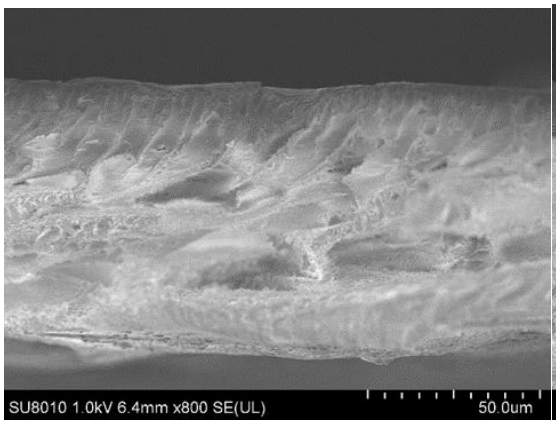
c 0.5%wt GO



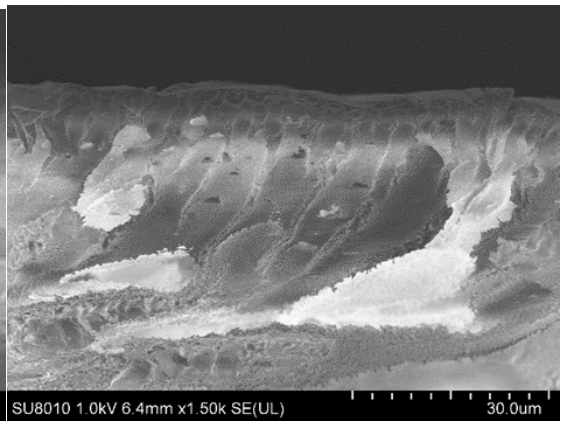
d 1.0%wt GO



e 1.0%wt GO

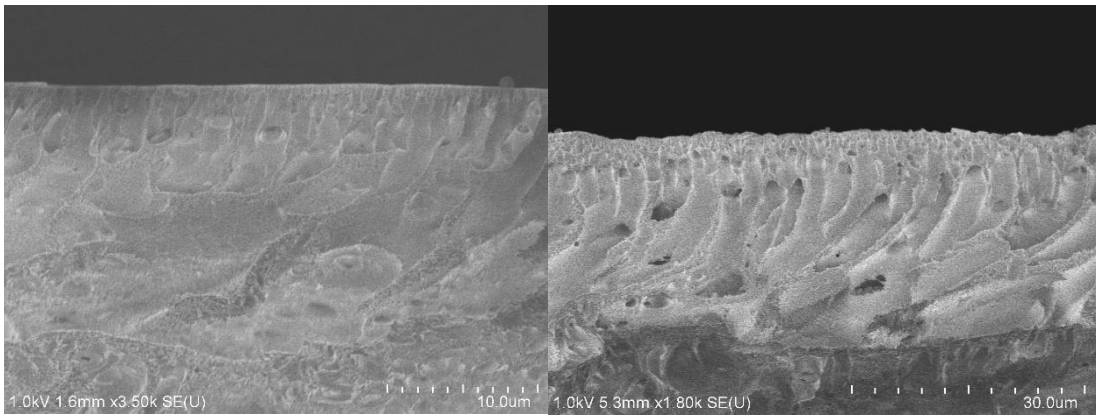


f 1.5%wt GO

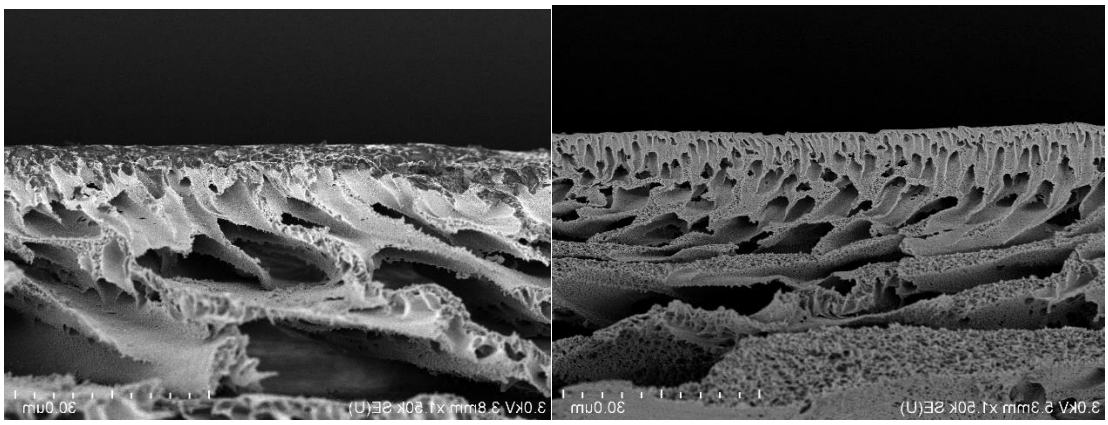


g 1.5%wt GO

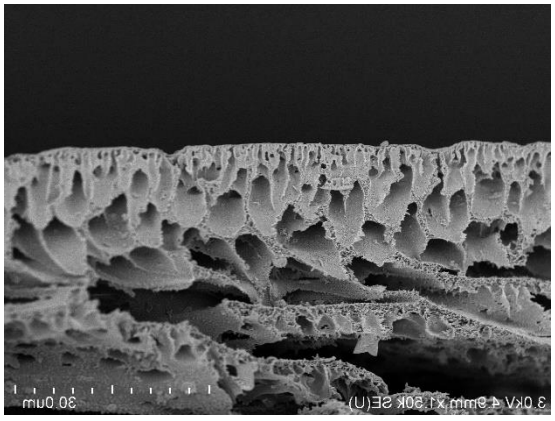
Figure 10 SEM pictures of PSf-GO at the GO content of 0%wt(a, b), 0.5%wt(c), 1.0%wt(d, e) and 1.5%wt(f, g). (GO content of 0.5%wt at 50μm could not get an evident image, so in the later MOS_2 image, I select these pictures)



h 0.05%wt MOS_2 i 0.1%wt MOS_2



j 0.2%wt MOS_2 k 0.5%wt MOS_2



l 1.5%wt MOS_2

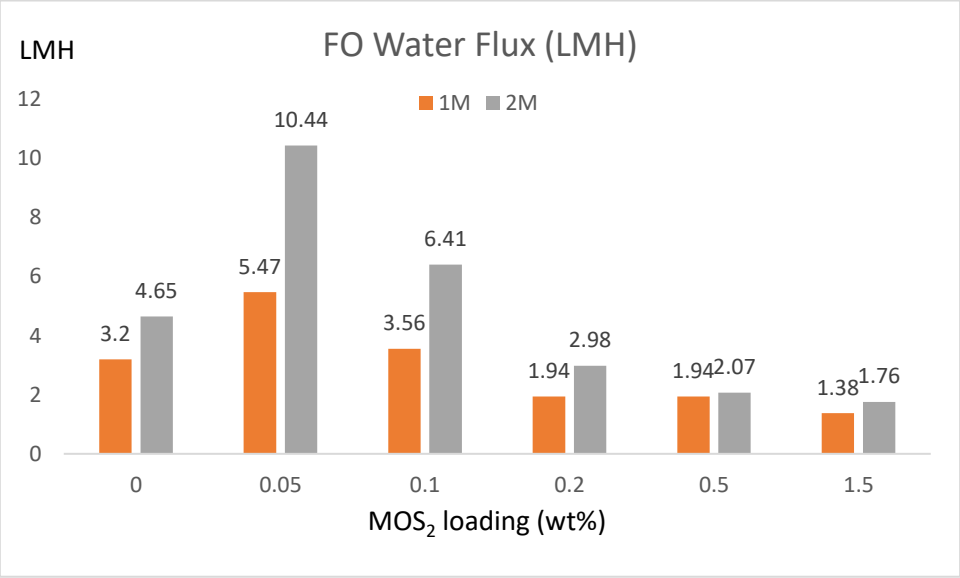
Figure 11 SEM pictures of PSF-MOS_2 at the MOS_2 content of 0.05%wt(h), 0.1%wt(i), 0.2%wt(j), 0.5%wt(k) and 1.5%wt(l)

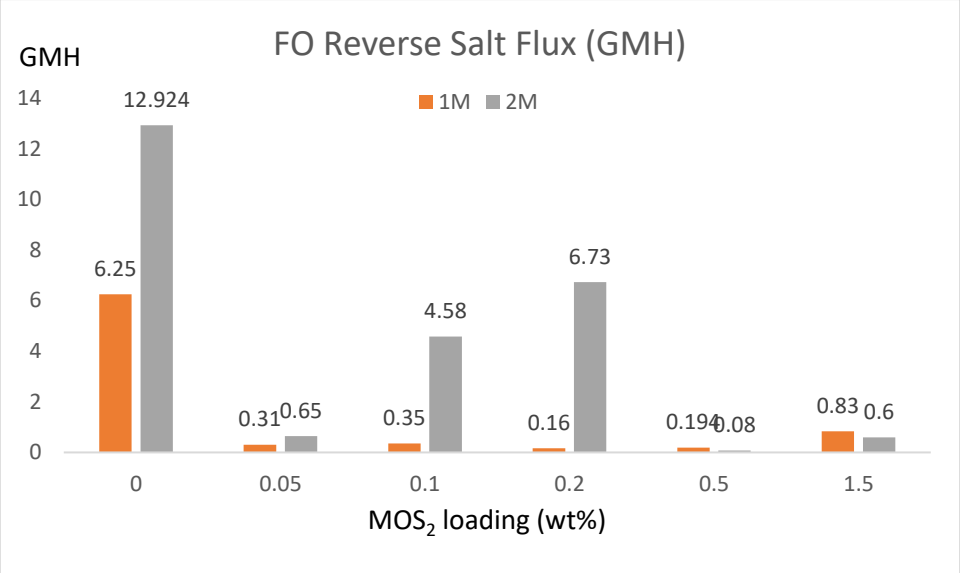
From Figure 10, the coating of GO had the similar impact

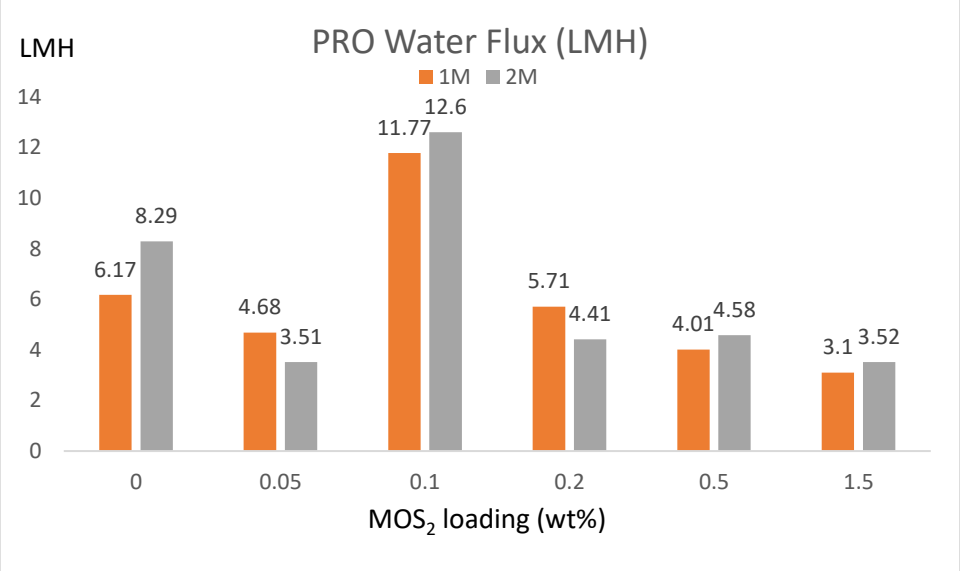
as MoS_2. The difference was that increasing coating amount favored the formation of better penetrated pore structure, as a separation membrane. The 1.5%wt GO coating provided the most penetrated cores as compared with the other concentrations. It exhibited a relatively higher degree of irregularities and more pores on the membrane surface. It was known from the SEM image that the high dosage of nanoparticles would be inevitably aggregated, and the removal of them may form a considerable of pores and/or cavities on the membrane surface.

Some conclusions can be draw from the SEM images in Figure 11 as that: (1) the loading of MoS_2 significantly affected the morphology of the membrane surface and cross-section; (2) the more loading of MoS_2, the pore structure was better. To get a penetrated pore which is favorable to get good performance and less fouling, we should keep the loading of MoS_2 up to a certain extent. Based on the results, the overloading and no loading of MoS_2 would lead to the bad performance.

4.1.3.2 Water flux and reverse salt flux


FO Water Flux (LMH)
LMH
1M
2M
12
10
8
6
4
2
0
3.2
4.65
5.47
10.44
3.56
6.41
1.94
2.98
1.94
2.07
1.38
1.76
0
0.05
0.1
0.2
0.5
1.5
MOS2 loading (wt%)


FO Reverse Salt Flux (GMH)
GMH
1M
2M
14
12
10
8
6
4
2
0
6.25
12.924
0.31
0.65
0.35
4.58
0.16
6.73
0.194
0.08
0.83
0.6
0
0.05
0.1
0.2
0.5
1.5
MOS2 loading (wt%)


PRO Water Flux (LMH)
LMH
1M
2M
14
12
10
8
6
4
2
0
6.17
8.29
4.68
3.51
11.77
12.6
5.71
4.41
4.01
4.58
3.1
3.52
0
0.05
0.1
0.2
0.5
1.5
MOS2 loading (wt%)

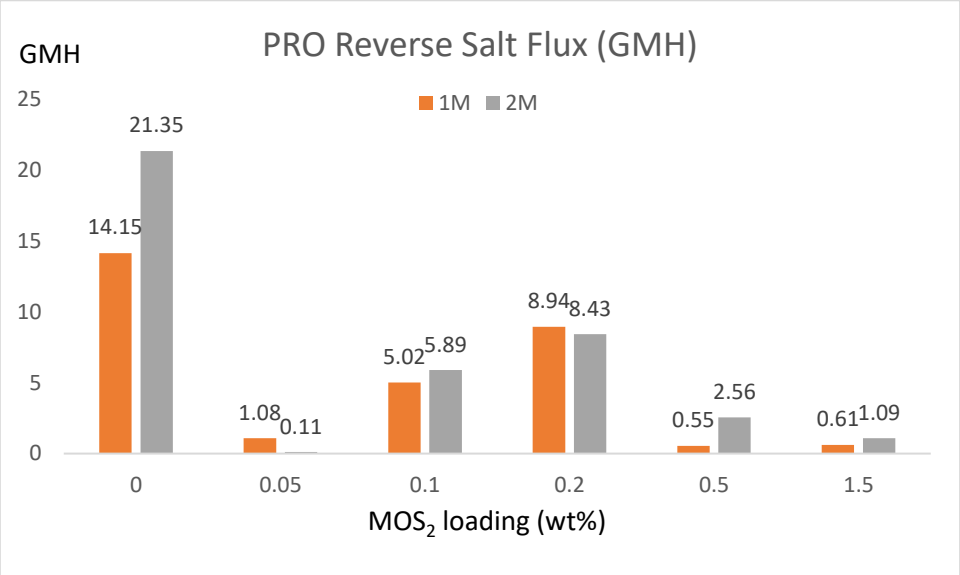


Figure 12 Membrane pure water flux and reverse salt flux results under 1M and 2M draw solution in FO and PRO systems.

In Figure 12, after adding MoS_2, pure water flux increased when 0.05%wt and 0.1%wt of MoS_2 are added into nanocomposite support layer in FO mode. 0.05%wt MoS_2-PSf-PA exhibited the best performance in FO mode with a pure water flux of 10.4 LMH under 2M NaCl draw solution with the reverse salt flux of 0.6 GMH. At this concentration, pure water flux increased two times higher than the transparent PSf membrane, and the reverse salt flux decreased by 95%. Overall, for both FO and PRO mode, pure water flux did not change obviously after adding excessive MoS_2. However, the reverse salt flux decreased a

lot. Almost all the membranes with MoS_2 exhibited very low reverse salt flux below 2 GMH. When MoS_2 loading was high, the reverse salt flux was always at a low level, but the flux was much smaller than a membrane. The conclusion was that, different from GO, the excess addition of MOS_2 was not favorable to enhance pure water flux, so the contents of 0.05%wt and 0.1%wt were the best.

4.1.3.3 XRD image of PSf-GO membrane

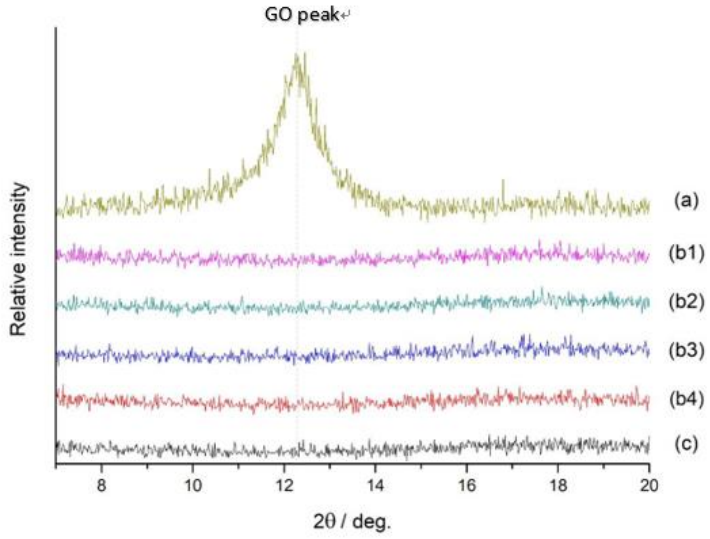


Figure 13 XRD result of PSf-GO membrane
(a) Pure GO (b1) 2.0%wt GO/ PSf (b2) 1.5%wt GO/ PSf (b3) 1.0%wt GO/ PSf (b4) 0.5%wt GO/ PSf (c) pure PSf

X-ray diffraction (XRD) was used to determine if GO sheets were present as individual GO sheets in the PSf-GO nanocomposite support layer or not. If so it means the GO was well blended in the support layer. The characteristic diffraction peak of GO locates at 2θ=12.3°. However, after GO was mixed into the PSf solution, the XRD pattern of PSf/GO GO peak at 2θ=12.3°disappeared. Even with the increasing of GO loading in PSf solution, the GO peak still not appeared again. This result indicated that GO was mainly presented as the individual GO sheets and incorporated into the polymer matrix.

4.1.3.4 FTIR result of PSf-GO

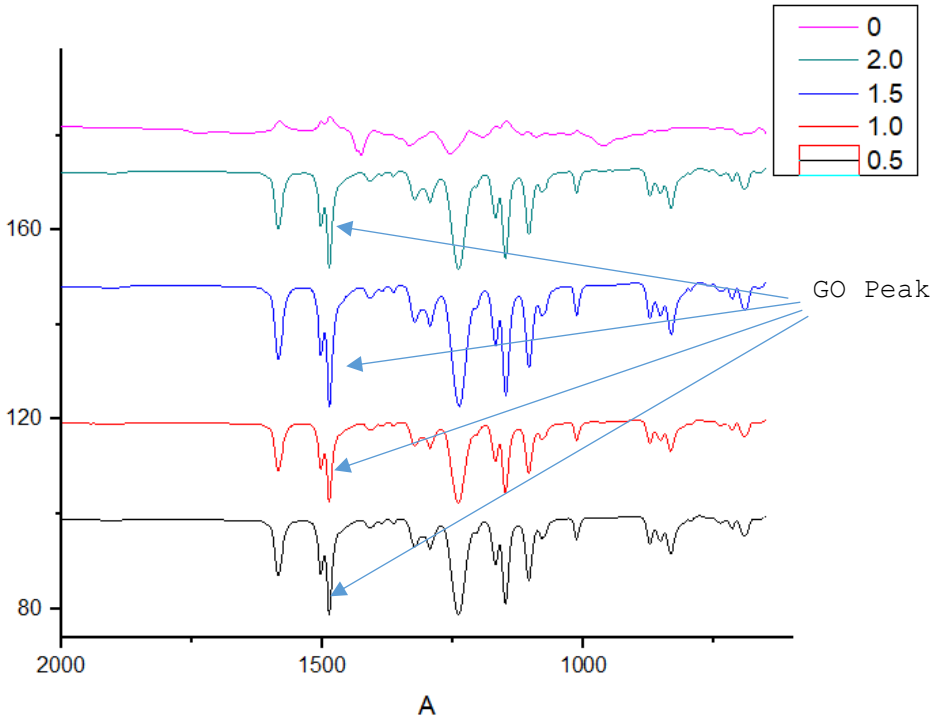


Figure 14 FTIR result of PSf-GO

From Figure 14, it could be found that the GO was welly blended with the PSF matrix because the characteristic adsorption peaks appeared at the similar location with the wave length of 1500cm^{-1}. On the contrast, the transparent membrane did not have the similar peaks in FTIR image.

CHAPTER 5

CONCLUSIONS

In this work, a new type of FO membrane was synthesized by blending nanoparticles GO and MOS_2 with PVDF and PSf membrane. Both two nanoparticles can be evenly and easily dispersed in NMP. The transport properties of all the thin film nanocomposite membranes with various GO and MoS_2 loadings were tested under both FO and PRO modes. The effects of GO and MoS_2 loadings were investigated to optimize the FO and PRO performance. Besides, the characterizations such as SEM, AFM and contact angle were also conducted to characterize the structures of both the support layer and the active layer of the membranes.

The application of FO was limited in the past decades due to the low water flux, high reverse salt flux, and irreversible fouling. This research provides a new method of incorporating nanoparticles, GO and MOS_2, into conventional membranes to enhance its FO performance under some certain conditions. It may have a great potential to be applied in a large scale FO membrane production.

CHAPTER 6

RECOMMENDATIONS

With the limitation of experience, there are many drawbacks to be improved in my work. I am going to be more cautious to avoid the previous mistake and put in more critical thinking in future work.

First part is the improvements in the fabrication process.

After many times work and refer to some articles, I find some details which would lead to the failure of the experiment. Aiming to these details, I could do efficient modification in my experiment:

1. The order is important! To disperse the nanoparticles firstly, and then add the polymer to the solution. Reversing the order is going to ruin the experiment.
2. On the stirring of PVDF and NMP, we must make the speed very fast at first to let the PVDF rinse entirely in the NMP and then adjust to a proper speed about 100r/min until the homogeneous solution was formed.

3. Getting rid of bubble must be finished before casting membrane, or the defects will appear. We will not have a second chance to remove it.

4. The temperature of the water does not significantly affect the membrane structure but may affect the phase inversion process.

5. The glass must be flat and dry. Because the thickness is not very large, so the rough surface will lead to the thickness difference. If the glass is wet, the phase inversion will happen on the glass on the wet part, the fabrication died.

6. For the time demand of phase inversion, it varies depending on the different materials. For PES-PA system, the time is 24h, for PSFN-PA system, the time is only 10mins, for PVC-LDH system, the time is 12h.

The second part is the improvements in active layer fabrication.

1. The MPD concentration usually in the range of 0.5-2.0%wt, TMC concentration generally in the field of 0.15-0.3%wt. We could adjust the concentration of two liquid according to the thickness we want.

2. Base on the different substrate material, we may have to do some pretreatment before the coating of PA, such as the PSf should be heated in a 70℃ water bath for 2min and then quenched in a 23℃ water bath to make the pore structure more compact and stable.

3. To get an ideal PA active layer, we cannot wipe and sweep the surface after pouring MPD, or it may lead to some invisible holes on the active layer.

The last part is the improvements of other blending nanoparticle materials such as carbon nanotubes (CNTs). Also, the membrane materials such as PVA or PVC could be an optional choice for the support layer. By the limitation of experiment condition and process, I have tried to make a PVA support layer blended with GO, but the result was not as I expect, so I did not try MoS_2 for another time.

APPENDIX A: RAW DATA

Table A-1 PVDF-GO water flux and reverse salt flux.

GO loading	FO flux		FO reverse salt flux		PRO flux		PRO reverse salt flux		
%	LMH		GMH		LMH		GMH		
	1M	2M	1M	2M	1M	2M	1M	2M	
0	3.2	4.65	6.25	12.924	6.17	8.29	14.15	21.35	0
1	4.12	5.51	1.66	1.925	6.71	9.7	1.08	1.96	0.5
2	6.33	7.17	0.97	2.27	3.46	4.87	0.9	1.5	1
3	5.46	5.71	2.27	1.44	3.33	5.714	1.19	1.49	1.5
4	4	7.87	0.75	0.87	3.7	5.19	1.16	2.38	2

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)
Long Name	GO/pvdf perce	0.5M	1M	1.5M	2M
Units	%				
Comments					
1	0	1.53	1.17	0.82	1.01
2	0.4	3.4	4.55	5.203	3.9819
3	0.8		58.91	81.16	90.22
4	1.2		69.36	63.59	54.01

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)
Long Name	GO percent	0.5M	1M	1.5M	2M
Units	%				
Comments					
1	0	2.35	3.25	4.03	6.08
2	0.4	6.27	5.49	7.05	12.49
3	0.8	--	5.41	8.47	12.54
4	1.2		46.68	63.59	--

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)
Long Name	GO percentage				
Units	%				
Comments		0.5M	1M	1.5M	2M
1	0	1.49			
2	0.2	3.53	1.53	2.55	1.69
3	0.4	3.647	6	5.25	7
4	0.6	3.73	--	2.98	2.71
5	0.8	4.03	8	6.7	7.49
6	1	3.06	2.27	3.53	5.33
7	1.5	1.64	11.43	11.64	7.96

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)
Long Name	GO percentage				
Units					
Comments		0.5M	1M	1.5M	2M
1	0	2.13			
2	0.2	43.52	87.22	120	154
3	0.4	9.92	28.27	31.13	27.96
4	0.6	198	--	368.63	323.14
5	0.8	28.6	61.18	106.75	149.48
6	1	142.86	151.04	365	490.6
7	1.5	227.64	370.93	592.6	313.7

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)	G(Y)	H(Y)	I(Y)	J(Y)
Long Name	GO loading	FO flux		FO reverse salt flux		PRO flux		PRO reverse salt flux		
Units	%	LMH		GMH		LMH		GMH		
Comments		1M	2M	1M	2M	1M	2M	1M	2M	
1	0	3.2	4.65	6.25	12.924	6.17	8.29	14.15	21.35	0
2	1	4.12	5.51	1.66	1.925	6.71	9.7	1.08	1.96	0.5
3	2	6.33	7.17	0.97	2.27	3.46	4.87	0.9	1.5	1
4	3	5.46	5.71	2.27	1.44	3.33	5.714	1.19	1.49	1.5
5	4	4	4.78	0.75	0.87	3.7	5.19	1.16	2.38	2

Table A-2: PVDF-MOS_2 water flux and reverse salt flux

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)	G(Y)	H(Y)	I(Y)	J(Y)
Long Name	MoS2 loading	FO flux		FO reverse salt flux		PRO flux		PRO reverse salt flux		
Units	%	LMH		GMH		LMH		GMH		
Comments		1M	2M	1M	2M	1M	2M	1M	2M	
1	1	3.2	4.65	6.25	12.924	6.17	8.29	14.15	21.35	0
2	2	5.47	10.44	0.31	0.65	4.68	3.51	1.08	0.11	0.05
3	3	3.56	6.41	0.35	4.58	11.77	12.6	5.02	5.89	0.1
4	4	1.94	2.98	0.16	6.73	5.71	4.41	8.94	8.43	0.2
5	5	1.94	2.07	0.194	0.08	4.01	4.58	0.55	2.56	0.5
6	6	1.38	1.76	0.83	0.6	3.1	3.52	0.61	1.09	1.5

Table A-3: Contact angle data

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)
Long Name	Time	0GO	0.4GO	0.8GO	1.2GO
Units					
Comments	second				
7	30	82.08	71.38	70.1	69.81
8	35	81.83	71.18	69.92	69.57
9	40	81.67	71.12	69.91	69.29
10	45	81.57	70.91	69.78	69.18
11	50	81.4	70.82	69.63	69.02
12	55	81.28	70.65	69.54	68.68
13	60	81.13	70.6	69.43	68.57
14	65	80.97	70.48	69.39	68.33
15	70	80.86	70.35	69.2	68.21
16	75	80.69	70.27	69.12	68.08
17	80	80.62	70.15	69.05	67.96
18	85	80.43	69.97	68.9	67.81
19	90	80.31	69.88	68.82	67.68
20	95	80.21	69.79	68.57	67.67
21	100	80.02	69.63	68.5	67.44
22	105	79.91	69.54	68.42	67.36
23	110	79.74	69.44	68.29	67.3
24	115	79.66	69.3	68.16	67.12
25	120	79.49	69.25	68.05	67.07
26	125	79.4	69.12	67.92	66.95
27	130	79.22	68.93	67.86	66.83
28	135	79.15	68.84	67.68	66.71
29	140	79	68.74	67.6	66.58
30	145	78.92	68.64	67.45	66.53

Table A-4: PVDF content impact on membrane performance

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)	G(Y)	H(Y)	I(Y)	J(Y)
Long Name	polymer concentration	0.5M	1M	1.5M	2M		0.5	1	1.5	2
Units										
Comments										
1	15	1.49								
2	17	5.96	1.53	2.39	1.88		2.31	3.06	2.94	3.41
3	20	1.53	1.17	0.82	1.01		1.41	1.52	2.23	2.51
4	--	--					--			
5		FO					PRO			

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)	G(Y)	H(Y)	I(Y)	J(Y)
Long Name		0.5M	1M	1.5M	2M		0.5	1	1.5	2
Units										
Comments										
1	15	2.13	--	--	--					
2	17	22.75	72	76.87	100.71		17.3	28.24	45.09	62.75
3	20	2.35	3.25	4.03	6.08		0.5	1.146	2.315	1.35
4	--	--					--			
5		FO					PRO			
6		rsf-reverse salt flux								

Table A-5: Thickness effects on membrane performance

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)	G(Y)	H(Y)	I(Y)	J(Y)
Long Name		0.5	1	1.5	2		0.5	1	1.5	2
Units										
Comments										
1	7	1.49	--	--	--		--	--	--	
2	8	4.235	2.588	3.725	3.059		2.15686	2	3.0588	3.49
3	9	3.529	2.275	2.078	6.784		0.78	5.373	5.3725	9.8039
4		--					--			
5		FO					PRO			

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)	G(Y)	H(Y)	I(Y)	J(Y)
Long Name		0.5M	1M	1.5M	2M					
Units										
Comments										
1	7	2.13	--	--	--	--	--	--	--	--
2	8	24.12	47.828	70.84	89.01	--	37.32	89.493	133.7255	167.3196
3	9	38.04	32.37	57.33	79.17	--	15.33	77.06	169.11	201.48
4		--					--			
5		--					--			
6		FO					PRO			
7		rsf-reverse salt flux								

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